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USE OF RHODAMINE B DYE AS A TRACER IN STREAMS OF THE SUSQUEHANNA RIVER BASIN

Goldberg, et al

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1.

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PURPOSE AND SCOPE

This paper relates the experiences of the Susquehanna Field Station - Chesapeake Bay-Susquehanna River Basins Project - in the use of Rhodamine B dye techniques in the stream environments of the Susquehanna River Basin. Particular problems encountered in the use of fluorescent tracer techniques, and the solution of many of these problems will be discussed. Instruments and equipment found most suitable for streams in the Susquehanna Basin are listed in Appendix I.

ACKNOWLEDGMENTS

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I. INTRODUCTION

The use of Rhodamine B, or similar fluorescent, organic dyes, for studying the physical characteristics of streams and bodies of water has become extensive since introduction of the technique by Carpenter[1]. These dyes are primarily used for studying "time of passage" and diffusion characteristics in estuaries[1], bays[2, 3], and streams[4, 5]. The technique involves use of a substance (dye in this case) which can be detected in very dilute concentrations by an instrument such as a fluorometer. The dye has physical properties which allow it to mix and be transported as an integral part of the water, effectively simulating movement of wastes or other materials introduced into the system.

The use of Rhodamine B dye in Susquehanna River Basin streams brought to light several problems not encountered when using the technique in other streams or in estuaries. The chemical composition, velocity, mixing, and current characteristics of streams were found to present unusual problems for analysis.

II. CONSIDERATIONS WHEN USING FLUORESCENT DYE TECHNIQUES

The use of fluorescent dye techniques requires consideration and evaluation of the following factors:

1. Instrument calibration and natural background
2. Hydrogen ion concentration
3. Temperature
4. Decomposition - oxidation, reduction, etc.
5. Sorption
6. Photochemical decay
7. Metal inhibition

Project use of Rhodamine B dye and the fluorometer produced several specific problems and solutions. Outlines of the problems encountered, along with the solutions found most satisfactory, are presented below.

Heat Transfer During Calibration

The use of submersible pumps in the calibration medium proved unsatisfactory because of gross heating of the medium from pump operation. The heat generated from the pump after repeated recirculation affected dye stability and caused fluorescence loss. To avoid this problem, a small centrifugal pump was utilized in the laboratory during instrument calibration. Submersible pumps

were quite satisfactory in field installations where recirculation was eliminated.

Dye Adsorption on Metal Parts of the Equipment

Metal parts, particularly copper and brass, exhibit a great affinity for the dye. Considerable difficulties arise from this adsorption and subsequent release of dye on equipment, as it interferes with calibration and evaluation of dye concentration during laboratory and field studies. The small centrifugal pump used during calibration was of an inert material, avoiding adsorption onto the pump during the long periods of recirculation. A pump having a primarily brass body was used in the field; however, contact time of the media with the pump was very short, and there was no recirculation. Inert materials such as polyethylene tubing and fittings were utilized both in the laboratory and in the field.

Type of Pump

A Little Giant Model 4-12NR submersible pump was unsatisfactory for field installation because of poor lift characteristics. A Demming Model 2ALF4-115V, 1/3 HP submersible pump provided the necessary capability.

Volume of Sample Through the Fluorometer Curvette

Sample volumes passing through the fluorometer curvette in excess of about 1.5 gallon/hour result in turbulent flow, with subsequent light scattering and instrument instability. Control of flow from the pump was accomplished by use of a manifold with a bleeder valve for gross volume control, in series with a needle valve for optimum adjustment. See Figure 1.

Power Supply

Power requirements for the field studies were initially supplied by a portable 4 HP, 13 ampere, 115 volt, AC generator. The fluorometer requires an AC power supply regulated between 105 and 130 volts for stable generation. This generator unit was found to be of insufficient capacity to provide power for the 1/3 HP sample pump and to maintain the constant voltage supply required for the fluorometer.

A possible solution was the use of separate power supplies for the pump and the fluorometer. This would require a DC-AC converter utilizing a 12 volt DC battery or generator; however, the converters are relatively expensive. To eliminate the converter and second power source, a Baker Heavy Duty 12v DC - 115v AC generator was installed on the Ford Econovan field vehicle in place of the standard 12 volt generator. This unit supplies the regulated 115 volt AC power for the fluorometer, pump, and lighting requirements, as well as 12 volt DC power for vehicle operation.

Interference Materials in the Streams

Some streams contain materials which fluoresce at the same wave length as the dye being used or within the band pass of the emission filter. This is particularly true of streams receiving pulp and paper mill wastes. The high background contributed from these materials in the stream mask and compromise the sensitivity of the method. Where low concentrations of dye which barely exceed the expected variations in background are used, high background becomes most problematical.

Effects of pH on Emission

It has been stated that Rhodamine B dye appears relatively stable over the pH range of 2 to 10; however, these limits were established in estuaries where the buffering capacity of the water is considerable. The Project found that emission is adversely affected at each end of this pH range, as streams in the study area did not have a large buffering capacity. Project experiments conducted in streams and on stream samples under laboratory conditions reveal a loss of emission below a pH of 4 and above a pH of 7. Emission loss does not appear quantitatively recoverable when the pH is adjusted, i.e., from 3.5 to 4.0 or from 7.5 to 7.1. This would indicate a reaction resulting in dye destruction, dye conversion to a form fluorescing at a different wave length, or formation of a non-fluorescing compound. An additional problem results from the dye having different solubilities at high and low pH.

pH is a very acute problem in the Susquehanna River Basin, and the ranges of pH discussed above are quite commonly encountered during passage of the dye in the streams.

Temperature

There was a loss of fluorescence with increasing temperature (approximately 2% with each degree Centigrade increased). With tap or distilled water, recovery of emission after cooling is essentially quantitative; however, when stream water was used as a substrate, emission recovery after a prior temperature rise was variable. This variability indicates a change in the dye composition may occur, which is a function of stream conditions and temperature.

Dye Loss at Power Stations

Dye passing through heat exchangers showed very high reductions in quantity or fluorescence upon return to the stream. Probable cause of the loss was dye decomposition at the high temperatures; however, adsorption and metal inhibition probably contributed to the problem.

Dye Adsorption in the Stream

Adsorption of dye in streams having significant amounts of suspended solids and/or obstructive matter is visually evident. This adsorption greatly affects the concentration of the dye front, as well as the time of resolution for the passage of the peak concentration. Also, the shape of the recovery curve is considerably affected, particularly as a result of the release of adsorbed dye.

Metal Inhibition in the Stream

Various metal ions, e.g., copper, aluminum, and zinc, are known to inhibit fluorescence emission. The extent of fluorescence inhibition from metal concentrations in the stream can be determined by comparing results with streams having low metal ion concentrations and low inhibition.

Limits of Dye Concentration

Fluorescence emissions of Rhodamine B dye are characteristically linear over a finite range of dye concentration. The lower limit of concentration is set by natural background or interfering substances in the sample medium. The upper limit of dye concentration is determined by the absorption of incident ultraviolet

light, with the consequent deviation from linearity. Where work is required at dye concentrations greater than the maximum range selection of the instrument, a neutral density filter may be used with the secondary filter to decrease sensitivity, i.e., extend the range of the fluorometer.

Estimation of amount of tracer required will be the function of the physical and hydrologic characteristics of the stream, assuming consideration has been given to the various inhibitory mechanisms which may be present. Mr. R. L. O'Connell, Director, Annapolis Field Station, Chesapeake Bay-Susquehanna River Basins Project, has suggested a method for estimating dye requirements. This information is contained in Appendix II. It should be noted that where amounts of dye may be critical, e.g., dispersion and/or comparison with previous studies, consideration should be given to the possible variation in dye content of the manufacturer's preparations. It is recommended that samples of the dye be compared with each other, compensating for differences as required. On this basis, the initial dye preparation used could be considered to be the reference standard.

OBSERVATIONS

I. As stream flow decreases, time for peak concentration resolution increases.

II. Both leading and following edges of the dye front become diffuse, causing an alteration in the shape of the concentration vs. time curve. This alteration results in a positive displacement in time of both the centroid of mass and the peak concentration.

III. Using a single injection of tracer, greater displacement and alteration of the shape of the curves are observed at stations downstream. Peak concentrations are decreased at downstream stations, and comparison of curves at various stations will serve to indicate diffusion and/or inhibitory characteristics of the reach of stream under consideration.

IV. The time of passage curve for dye may be used to estimate the time of arrival and probable concentration of waste at a given point from a single waste injection, such as an accidental spill. The leading and following edges of the curves can be used to estimate duration of critical or emergency conditions in the stream.

V. At present, there appears to be little exploratory work on other light fast tracers. It is suggested that lignin and/or lignin derivatives might be investigated. These compounds fluoresce at the same wave length as the Rhodamines, and, based on their method of preparation, these compounds might be applicable for use in both acidic and normal stream environments.

VI. It is essential that a field reconnaissance be made, sites selected, and the stream sampled for calibration and water quality to determine the feasibility of use of a tracer. Further determinations should be made at this time for auxiliary equipment requirements.

VII. Estimated time of travel should be established for the reaches under consideration, in order to reduce excessive time requirements in the field.

VIII. Injection of the dye into the environment should be accomplished in such a manner to insure immediate maximum dispersion. Addition of concentrated dye preparation without dilution may result in incomplete dispersion, particularly in shallow streams, with consequent undesirable effects on

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visualization of both the dye front and the shape of the time of passage curves.

IX. An analysis of peak dye concentration should be made at the first and each succeeding station to determine if enough dye exists to insure a measurable quantity at the next station downstream. If dye additions are necessary, they should be made at the time of peak concentration.

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APPENDIX I

INSTRUMENTS AND EQUIPMENT FOUND MOST SUITABLE FOR STREAMS IN THE SUSQUEHANNA BASIN

I. Fluorometer - All measurements utilized the Turner Model 111 fluorometer equipped with a 20 millimeter continuous flow curvette door and recorder.

II. Pump - In the field, a 1/3 HP Demming Model 2ALF4 - 115V submersible pump was utilized.

III. Power Supply - A Baker Heavy Duty generator was used to provide 115 volt AC power for instrument, pump, and lighting requirements, plus 12 volt DC power for vehicle operation.

IV. Laboratory - A modified Ford Econovan provides mobility and basic laboratory capability, including cabinets, sink, and sufficient counter space for the fluorometer and its accessories.

V. Irradiation Lamp - Maximum sensitivity was obtained using a G. E. G4T4/1 lamp as a light source, plus the proper excitation and fluorescence filters.

APPENDIX II

ESTIMATION OF DYE REQUIREMENTS FOR TIME OF TRAVEL STUDIES

An instantaneous release of dye to a river is planned to determine travel between two points. To find the amount of dye to be released,

$$M = \frac{CA(NX)^{1/2}R^{5/12}}{1.1(10^3)}$$

M = Weight of dye in grams

Where:

Cx = Peak concentration desired at downstream point x parts per billion

X = Distance between release and monitoring points in feet

A = Cross sectional area of stream at release point in square feet

R = Mean depth of stream between release and monitoring points

N = Manning's coefficient n for stream roughness

For example, in a stream where:

Width = 100 feet

Depth = 4 feet

Cx = 2.0 ppb (approximately 100 on 30 x scale for Rhodamine B)

X = 3 miles

R = 4 feet

N = 0.04

APPENDIX II (Continued)

$$M = \frac{2(100)4(0.04x3x5280)^{1/2}(4)^{5/12}}{1.1x10^3}$$

M = 32.6 grams required assuming 100% dye content by weight

Use M = 33 grams

Dye to be used: Rhodamine in Acetic Acid - 40% (weight basis) - sp. grav. 1.12

Volume of dye (V) = $\frac{33}{(1.12)(.40)}$ = 73 milliliters

Use 75 milliliters

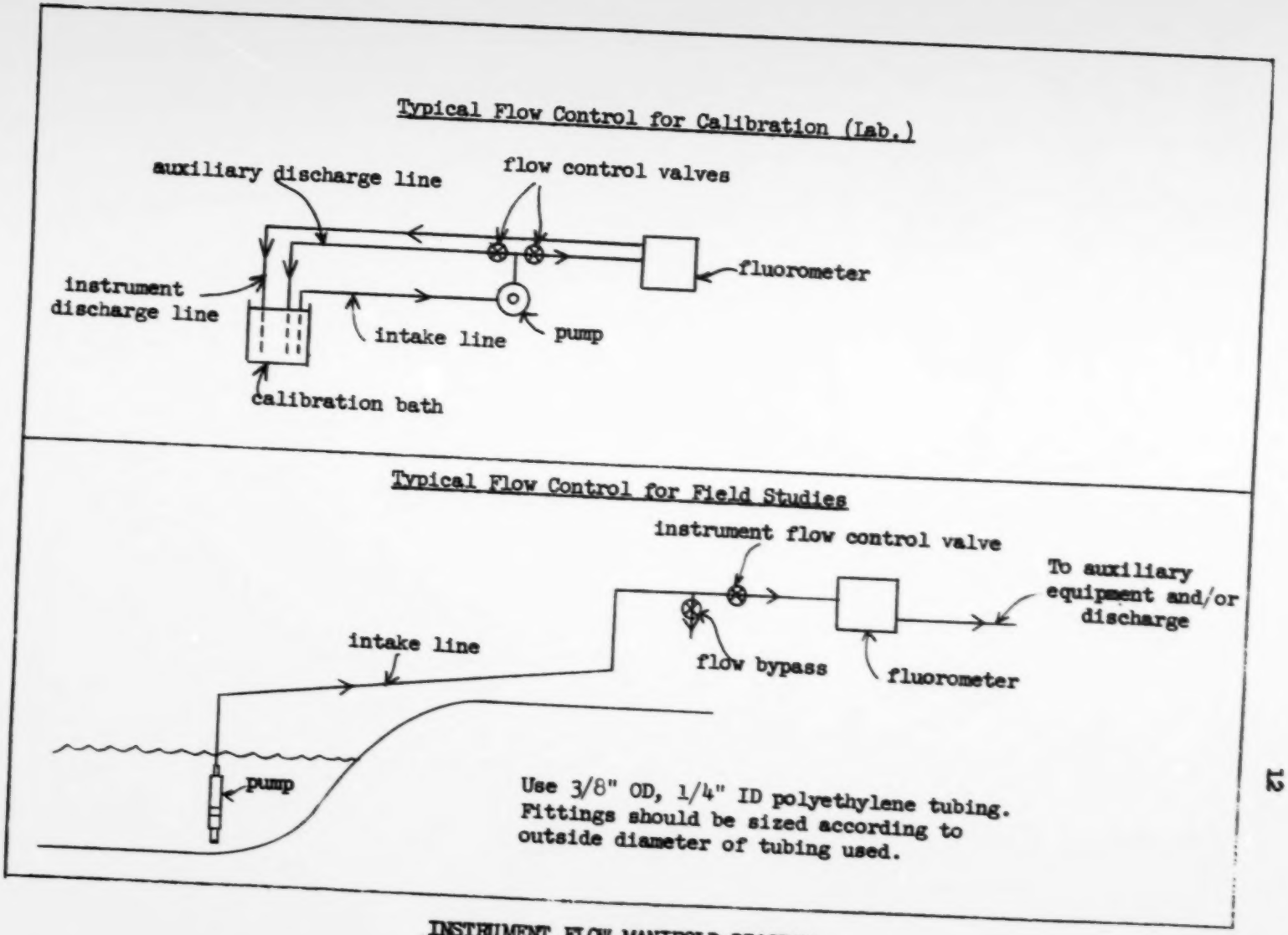

Figure 1

INSTRUMENT FLOW MANIFOLD DIAGRAM